

The University of Chicago.

Founded by JOHN D. ROCKEFELLER.

On Undecylamine and Pentadecylamine
and the Preparation of the Higher
Amines of the Aliphatic Series.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS
OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY ELIZABETH JEFFREYS.

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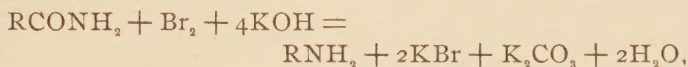


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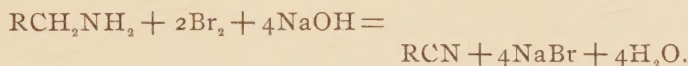
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On Undecylamine and Pentadecylamine and the Preparation of the Higher Amines of the Aliphatic Series.¹

Hofmann's² method of preparing amines by the action of bromine and potassium hydrate upon acid amides in aqueous solution according to

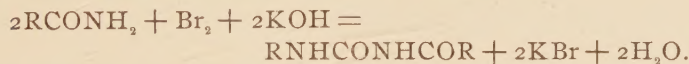


furnishes very good yields of the lower aliphatic amines, but as the molecular weight of the acid amide increases the yield of amine diminishes. This is due particularly to two secondary reactions, in one of which the bromine and alkali act upon the amines formed and produce nitrils according to the equation:



By distilling the amine with steam as soon as it is formed, Hoogewerff and Van Dorp³ succeeded in preventing the formation of nitrils.

In the other secondary reaction by which the yield of amine is diminished, acyl-alkylureas are formed:



With increasing molecular weight of the acid amide, the formation of these acylureas is favored and in the higher series they are the chief product of the action of bromine and aqueous alkali on acid amides. By saponifying such ureas amines can be obtained, but the yield is small.

¹ Vide also a preliminary report, Ber. d. chem. Ges., 30, 898.

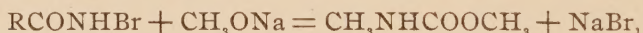
² Hofmann: Ber. d. chem. Ges., 15, 762.

³ Hoogewerff and Van Dorp: Rec. trav. chim., 6, 387.

Amines higher in the series than heptylamine cannot be obtained with good yields by the Hofmann method. To prepare octylamine, Hoogewerff and Van Dorp¹ distilled the bromamide with lime and obtained 45 per cent of the theoretical yield of amine. This method involves the preparation of the bromamide and, as shown below, this is one of the main difficulties to overcome in the higher aliphatic series. Hoogewerff and Van Dorp's method in modified form is hardly feasible, therefore, for preparing amines of very high molecular weight.

Turpin² prepared heptadecylamine, $\text{CH}_3(\text{CH}_2)_{16}\text{NH}_2$, by converting stearic amide by means of aqueous potassic hydrate and bromine into stearyl-heptadecylurea and distilling the urea with lime. As but half the urea molecule is of avail in preparing the amine, the yield obtained was necessarily low (22 grams of heptadecylamine from 100 grams of stearamide), and as a ketone, stearon, is also formed in the same reaction, the isolation of the pure amine involves a tedious process.

Lengfeld and Stieglitz³ having found that sodium methylate in methyl alcohol solution converts acid bromamides into urethanes according to



the work described in this paper was undertaken at the suggestion and carried on under the direction of Professor Stieglitz, to determine whether this reaction could not be utilized as a convenient method of preparing higher aliphatic amines, and also to determine, if possible, why, in the Hofmann reaction, the formation of ureas of the higher aliphatic series should be more favored than those of lower molecular weight.

The investigation was carried on by the use of palmitic, stearic, and lauric amides. All attempts to prepare palmitic and stearic bromamides proved unsuccessful.

The chloramides were, however, prepared with considerable difficulty and converted by treatment with sodium methylate into urethanes. As the preparation of the chloramides proved

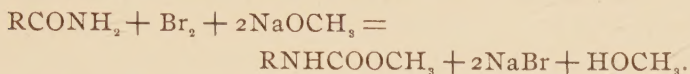
¹ Rec. trav. chim., **6**, 387.

² Ber. d. chem. Ges., **21**, 2488.

³ Am. Chem. J., **15**, 215, 504; **16**, 270.

so difficult, an attempt was made to effect a rearrangement of the amides in alcohol solution without the isolation of the chlor- or bromamides.

The experiments proved successful, urethanes being formed in almost quantitative yield according to

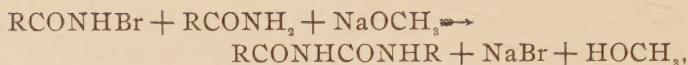


As amines were obtained in excellent yield when the urethanes were distilled with lime, the investigation has proved entirely satisfactory in leading to as convenient a method of preparing the higher aliphatic amines, as that employed in obtaining the lower amines.

From the easily accessible lauric and palmitic amides, the hitherto unknown normal undecylamine and normal pentadecylamine were prepared in considerable quantity; and from undecylamine, undecyl alcohol, also heretofore unknown, was prepared.

In regard to the second object of investigation, it was soon found that in order to prevent the formation of urea, it is necessary that a rearrangement shall take place quickly, almost instantaneously, throughout the whole mass. In working with lauric amide, it was found necessary to mix the substances together as quickly as possible. When the sodium alcoholate solution was poured in small quantities into the flask containing the solution of amide and bromine, two-thirds of the product was found to be urea. The same result was obtained when the amide and sodium alcoholate solutions were mixed together and the bromine added, drop by drop, to the mixture. If, on the other hand, the sodium alcoholate solution was poured, all at once, into the bromine and amide solution, almost a quantitative yield of urethane was obtained.

Apparently when the reaction proceeds slowly, one molecule of the bromamide after suffering the Beckmann rearrangement, unites at once with a second molecule of acid amide which is still present under those conditions, to form urea according to:



rather than with the alcohol to form a urethane.

The cause, therefore, of the formation of ureas when the higher amides are treated with bromine and aqueous alkali, according to Hofmann's method, lies undoubtedly in the fact, that, on account of their difficult solubility in aqueous solvents, the rearrangement of the acid amide takes place so slowly that there is always present a sufficient amount of amide to form a urea.

The inevitable conclusion to be drawn from the facts given was rather surprising, inasmuch as isocyanates, the probable intermediate products¹ in the Beckmann rearrangement,² under ordinary conditions, react much more readily with alcohols than with acid amides. Experiments were made by treating benzamide, in methyl alcohol solution, with phenyl isocyanate under varying conditions, and they invariably resulted in the formation of methylphenylurethane, not a trace of phenylbenzoylurea being formed.

According to Hoogewerff and Van Dorp bromformamides are the first intermediate products of the Beckmann rearrangement of acid bromamides, but chlorformanilide with a methyl alcohol solution of benzamide, under varying conditions, did not give any more phenylbenzoylurea than the isocyanate itself.³

The new method of converting acid amides into urethanes, by the action of bromine and sodium methylate, was found also to be applicable to the amides of the aromatic series. Since much time and labor are saved and the loss involved in the isolation of the dry bromamides is prevented, we can now class the urethanes among the most easily accessible bodies.

This method was also tried in cases where the old method had either failed entirely or given poor results. The yields

¹ Hofmann : Ber. d. chem. Ges., **15**, 412. ² Stieglitz : Am. Chem. J., **18**, 751.

³ The question raised will be further investigated as it promises to throw more light on the theory of the Beckmann rearrangement of acid bromamides. Mr. Yates is studying the action of undecyl isocyanate on lauric amide, as lauric amide seems to show a marked tendency to form undecyllaurylurea when subjected to the action of the rearranging reagents.

of urethanes obtained in ethyl alcohol solution were very much higher than those obtained by Swartz,¹ by the older method, but all attempts to effect a rearrangement of unsaturated acid amides, $RCH:CHCONH_2$, failed, because the unsaturated group is more reactive than the acid amide group.

For a similar reason salicylic amide, on account of the activity of the hydrogen of the benzene ring, due to the presence of the hydroxyl group, undergoes no rearrangement until the benzene ring has been brominated.

Experimental Part.

That acid chloramides can be used instead of acid bromamides in effecting the rearrangement to urethanes, was shown by the action of sodium methylate on benzchloramide. 1.2 gram (1 mol.) of benzchloramide was added to a solution of sodium methylate, obtained by dissolving 0.3 gram (2 atoms) of sodium in 12 grams of pure methyl alcohol. The reaction was complete after heating the mixture about five minutes on the water-bath. The excess of alkali was neutralized by acetic acid, the alcohol distilled and the residue recrystallized from hot water. The product obtained was identified by its melting-point (47°) and other properties as methylphenylurethane. The reaction takes place exactly as when benzbromamide is used.²

Palmitic Chloramide, $C_{16}H_{31}CONHCl$.—On account of the difficult solubility of palmitic amide, it was impossible to prepare palmitic bromamide, but the chloramide can be obtained in almost pure condition as follows: 10 grams of palmitic amide dissolved in about 400 cc. of alcohol were poured into about five times the calculated amount of hypochlorous acid, the acid having been prepared by passing chlorine into a 15 per cent solution of sodium carbonate, kept at a temperature of about -5° . A white precipitate was immediately formed, this being, evidently, the palmitic amide precipitated by the cold hypochlorous acid solution. Upon shaking the flask vigorously for a few minutes considerable heat was developed and the precipitate redissolved. On cooling, a white precipi-

¹ Am. Chem. J., 19, 295.

² Ber. d. chem. Ges., 19, 2274.

tate was deposited; this was filtered immediately and washed with a little ice-cold water. After it was dried on a clay plate for two or three hours, a chlorine determination was made by adding potassium iodide to an alcoholic solution of the chloramide, and acidifying and titrating with thiosulphate, the iodine being liberated according to:



I. 0.2046 gram substance gave 0.0238 gram chlorine.

II. 0.2026 gram substance gave 0.0236 gram chlorine.

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NOCl}$.	I.	Found. II.
Cl	12.26	11.65	11.65

Palmitic chloramide melts at 70° – 71° . It is insoluble in water, difficultly soluble in cold alcohol and ligroin and readily soluble in benzene, chloroform and ether. The yield is almost quantitative.

Methyl Pentadecylcarbamate, $\text{C}_{15}\text{H}_{31}\text{NHCO}_2\text{CH}_3$, from *Palmitic Chloramide*.—To convert palmitic chloramide into urethane 5 grams of it was treated with 0.45 gram of sodium dissolved in 18 grams of methyl alcohol. The chloramide dissolved immediately in the alkaline solution, but it was necessary to boil the solution for twenty minutes before the action was complete. After distilling off the alcohol, the product remaining was washed with water and recrystallized from hot alcohol.

I. 0.4406 gram at 739.8 mm. and 23.5° gave 19.8 cc. nitrogen.

II. 0.4568 gram at 744.7 mm. and 22.5° gave 21.3 cc. nitrogen.

III. 0.1992 gram gave 0.5208 gram CO_2 , and 0.2274 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NHCO}_2\text{CH}_3$.	I.	Found. II.
N	4.91	4.92	5.16
C	71.57	71.30	..
H	12.28	12.68	..

Methylpentadecylurethane is difficultly soluble in cold ligroin and in alcohol, but readily soluble in ether, chloroform and benzene. It crystallizes in leaflets and melts at 61° – 62° .

Preparation of Urethanes Directly from Amides.

As the isolation of the chloramide proved to be very difficult, the following experiments were made to convert acid amides directly into urethanes without isolating the chlor- or bromamides.

Methyl Phenylcarbamate, $C_6H_5NHCOOCH_3$.—A solution of 3.8 grams (2 equiv.) of sodium in 95 grams of methyl alcohol was poured into a flask containing 10 grams of benzamide (1 equiv.), dissolved in 51 grams of methyl alcohol, and to this mixture, 13.2 grams (2 equiv.) of bromine were added. Some action took place in the cold, but it was necessary to heat the mixture for twenty minutes before the action was complete.

After recrystallization from hot water 5.9 grams of pure urethane were obtained. The reaction takes place in the same manner when the sodium methylate solution is added to the mixture of amide and bromine solution.

Methyl m-Nitrophenylcarbamate, $NO_2C_6H_4NHCOOCH_3$.—3.8 grams (1 equiv.) of *m*-nitrobenzamide were dissolved in 16 grams of methyl alcohol, and to this were added 4 grams (2 equiv.) of bromine and 1.1 gram (2 equiv.) of sodium dissolved in 28 grams of methyl alcohol. The alcohol was allowed to evaporate at ordinary temperature and the residue shaken up with hydrochloric acid, to remove the small quantity of *m*-nitraniline formed, and then recrystallized from chloroform. The urethane was recognized by its crystal form and melting-point (147° – 149°) as being identical with the one obtained by Folin.¹ The yield obtained was 91 per cent of theory.

Methyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOCH_3$, from *Palmitic Amide*.—25.5 grams (1 mol.) of palmitic amide, dissolved by warming in 69 grams of methyl alcohol, were mixed with a solution of 4.6 grams (2 atoms) sodium in 115 grams of methyl alcohol and 16 grams (1 mol.) of bromine added.

¹ Folin; Am. Chem. J., 19, 323.

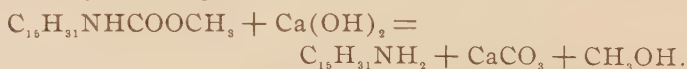
The mixture was heated on the water-bath for about ten minutes. After adding a few drops of acetic acid to neutralize the excess of alkali, the alcohol was distilled off, and the remaining product washed thoroughly with water to remove the sodium bromide. It was then dissolved in ligroin to separate the urethane from some unchanged palmitic amide (m. p. 104°), which is difficultly soluble in ligroin. When recrystallized twice from alcohol, the urethane melted at 61° – 62° , agreeing with that of the pentadecylurethane obtained by the action of sodium methylate upon palmitic chloramide. The yield is 83–94 per cent of the calculated quantity.

Its identity was further shown by an analysis.

0.383 gram at 752.6 mm. and 21.5° gave 17.9 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOOCH_3$.	Found.
N	4.91	5.25

Normal Pentadecylamine, $CH_3(CH_2)_{14}NH_2$.—Pentadecylamine can be prepared by heating pentadecylurethane with concentrated hydrochloric acid (five hours in a sealed tube to 200°) or with concentrated sulphuric acid (one hour to 110° – 120° in an open flask) and then heating with alcoholic potash and distilling. The best method of preparing the amine is to distil the urethane with about three and one-half times its weight of slaked lime, the amine being obtained quantitatively according to the equation :



Pentadecylamine Hydrochloride, $CH_3(CH_2)_{14}NH_3Cl$.—This salt is best prepared by dissolving the free amine (obtained by distilling pentadecylurethane with lime) in alcohol, adding an excess of concentrated hydrochloric acid, and evaporating to dryness on the water-bath. It was purified by washing it thoroughly with ether, then dissolving it in a small quantity of alcohol and precipitating with ether.

I. 0.3446 gram substance at 750.3 mm. and 23° gave 17.2 cc. nitrogen.

II. 0.4086 gram substance at 747 mm. and 16° gave 19.5 cc. nitrogen.

III. 0.2788 gram substance gave 0.6990 gram CO_2 , and 0.328 gram H_2O .

IV. 0.2244 gram substance gave 0.5604 gram CO_2 , and 0.2659 gram H_2O .

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NH}_3\text{Cl}$.	I.	Found. II.
N	5.31	5.55	5.43
C	68.31	68.37	68.10
H	12.90	13.07	13.16

Pentadecylamine hydrochloride crystallizes in glistening leaflets; it is very soluble in alcohol, but insoluble in ether, ligroin, and water. It decomposes without melting at 200° .

Pentadecylamine Chlorplatinate, $(\text{C}_{15}\text{H}_{31}\text{NH}_3)_2\text{PtCl}_6$, was prepared by adding a solution of chlorplatinic acid to an alcoholic solution of pentadecylamine. A yellow body was precipitated which is slightly soluble in alcohol, insoluble in water and decomposes without melting when heated above 205° .

0.5356 gram gave 0.1218 gram of platinum.

	Calculated for $(\text{C}_{15}\text{H}_{31}\text{NH}_3)_2\text{PtCl}_6$.	Found.
Pt	22.57	22.73

Monopentadecylurea, $\text{C}_{15}\text{H}_{31}\text{NHCONH}_2$. — The monourea furnishes an easy method for the rapid and certain identification of pentadecylamine or its hydrochloride. Molecular quantities of pentadecylamine hydrochloride dissolved in alcohol, and potassium cyanate, dissolved in as small a quantity of water as possible, were mixed together and evaporated to dryness on the water-bath. The compound formed was washed with water and recrystallized from hot alcohol.

0.2158 gram substance at 747.1 mm. and 21.5° gave 20.2 cc. nitrogen.

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NHCONH}_2$.	Found.
N	10.37	10.45

Monopentadecylurea is a white substance crystallizing in leaflets and melting at 109° ; it is insoluble in ligroin but readily soluble in hot alcohol. It was used most frequently in identifying the new amine.

Pentadecylamine, $\text{CH}_3(\text{CH}_2)_{14}\text{NH}_2$.—The free amine is best prepared as follows: 70 grams of lime, to which has been added 30 grams of water and 20 grams of pentadecylurethane are thoroughly mixed together and distilled from a porcelain, or hard glass retort of 300 cc. capacity. The receiver was kept in cold water. The product formed was dissolved in ligroin, and dried with caustic potash. The ligroin solution was separated from the caustic potash by filtering it with a siphon filter. The amine was then heated on the water-bath for a couple of hours over sodium, and finally distilled over sodium into a second distilling-flask, from which it was redistilled.

I. 0.3488 gram at 751.8 mm. and 13.7° gave 17.1 cc. nitrogen.

II. 0.4186 gram at 735.4 mm. and 15.5° gave 21.1 cc. nitrogen.

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NH}_2$.	I.	Found.
N	6.16	5.75	II. 5.69

When the free amine is weighed it absorbs carbon dioxide and water from the air with such avidity that it is impossible to get very good figures. In order to obtain a more exact analysis, the specimen analyzed was converted into the hydrochloride, and a determination of the hydrogen, carbon and nitrogen made (see second analysis of pentadecylamine hydrochloride).

Pentadecylamine is a white substance crystallizing in leaflets, melting at 36.5° and boiling at 298° – 301° at ordinary pressure; it has a peculiar odor, dissolves in all the organic solvents, and combines with acids, but does not dissolve in them. By working carefully, almost a quantitative yield can be obtained.

Benzoylpentadecylamine, $\text{C}_{15}\text{H}_{31}\text{NHCOC}_6\text{H}_5$.—A calculated quantity (1 mol.) of benzoyl chloride was added to an ether solution of pentadecylamine (2 mol.). In order to get all the amine in solution, it was necessary to heat it to drive off any carbon dioxide absorbed, as the carbonate is not soluble in ether. The ether mixture was shaken up with a weak solution of caustic soda and when no further odor of

benzoyl chloride was perceptible, it was washed two or three times with water and the ether distilled.

The compound obtained crystallizes in needles and melts at 78° ; it is soluble in ether, alcohol and benzene.

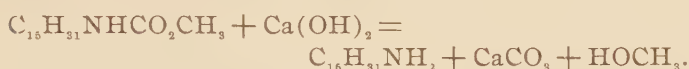
For analysis it was recrystallized from benzene.

I. 0.4552 gram substance at 743.3 mm. and 17° gave 18.2 cc. nitrogen.

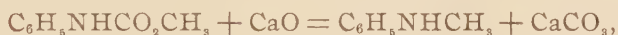
II. 0.4368 gram substance at 746.1 mm. and 17.3° gave 17.1 cc. nitrogen.

	Calculated for $C_{16}H_{31}NHCOC_6H_5$.	I.	Found.
N	4.22	4.59	4.44

All the analytical data obtained for the compound formed when pentadecylurethane is distilled with slacked lime, as well as those obtained for its derivatives, indicate that it is a primary amine formed according to:



As Nölting¹ observed that methylphenylurethane, $C_6H_5NHCOC_2H_5$, gives on distilling with lime (unslacked) monomethylaniline according to:

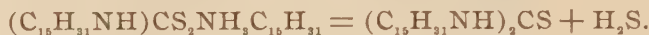


and the analytical figures for derivatives of pentadecylamine, $C_{16}H_{31}NH_2$, and methylpentadecylamine, $C_{16}H_{31}NHCH_3$, lie rather close together, some reactions were tried which prove beyond any doubt that the amine prepared by me is a primary amine; with carbon disulphide it gives a mustard oil, $C_{16}H_{31}N=CS$; by the action of phosgene the isocyanate, $C_{16}H_{31}NCO$, is obtained and by the action of sodium nitrite on the hydrochloride of the amine, it is converted into normal primary pentadecyl alcohol, $C_{16}H_{31}OH$.

Pentadecylamine Pentadecyl Dithiocarbamate, $(C_{16}H_{31}NH)CS_2NH_2$, was obtained when an excess of carbon disulphide was added to an ether solution of pentadecylamine. A white precipitate was at once formed, which, when filtered and dried, melted at 99° . The substance was not analyzed, but was heated in a sealed tube for twenty hours at 100° .

¹ Ber. d. chem. Ges., 21, 3155.

Hydrogen sulphide was split off, and the dithiocarbamate converted into dipentadecylthiourea according to :

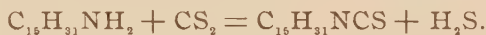


Dipentadecylthiourea was recrystallized by dissolving it in alcohol and precipitating it with water. It melts at 88.5° .

0.2142 gram gave 0.0984 gram barium sulphate (Carius' method).

	Calculated for ($\text{C}_{15}\text{H}_{31}\text{NH}$) ₂ CS.	Found.
S	6.45	6.30

Pentadecyl Mustard Oil, $\text{C}_{15}\text{H}_{31}\text{NCS}$, was prepared by heating pentadecylamine in solution in absolute alcohol with an excess of carbon disulphide :



This simple method seems to be a general one for preparing mustard oils from the higher aliphatic amines, since it succeeded with pentadecylamine as well as with heptadecylamine.¹ It was necessary to boil the alcoholic mixture for two days, at the end of which time no further odor of hydrogen sulphide could be detected. On evaporating the alcohol, a solid and an oil remained in the flask. The oil was dissolved in ligroin, and the solid remaining undissolved was identified as dipentadecylthiourea (m. p. 88.5°). As the oil was found to be impure and as it decomposes on distilling *in vacuo*, no analysis of the compound could be obtained, but it was identified as being chiefly pentadecyl mustard oil, $\text{C}_{15}\text{H}_{31}\text{NCS}$, by its action on amines. With aniline it gives phenylpentadecylthiourea according to :



and warmed with pentadecylamine, it yields dipentadecylthiourea.

Phenylpentadecylthiourea, $\text{C}_{15}\text{H}_{31}\text{NHCSNHC}_6\text{H}_5$, was obtained when molecular quantities of the mustard oil, dissolved in alcohol and aniline, were mixed together, and the solution boiled for ten or fifteen minutes on the water-bath. A few drops of acetic acid were added and the alcohol distilled. After recrystallizing the residue several times from alcohol, the thiourea obtained was found to melt at 79° .

¹ Turpin: Ber. d. chem. Ges., 21, 2486.

The same compound was also prepared by adding to pentadecylamine the calculated amount of phenyl mustard oil, and heating the mixture for a few minutes on the water-bath. After recrystallizing from alcohol, the substance obtained by this method was found to melt at 79° . A mixture of the two melted sharply at 79° , showing them to be identical and leaving no doubt as to the constitution of the thiourea.

0.267 gram substance at 24° and 747 mm. gave 19 cc. nitrogen.

	Theory for $C_{29}H_{38}N_2S$.	Found.
N	7.73	7.84

To convert the mustard oil into dipentadecylthiourea, it was added to a calculated quantity of pentadecylamine, dissolved in alcohol, and heated for a short time. The thiourea obtained in this manner, when recrystallized from alcohol, melts at 88.5° and agrees in every respect with the dipentadecylthiourea previously prepared.

Pentadecylurea Chloride, $C_{15}H_{31}NHCOCI$.—An effort was made to obtain the urea chloride by the method employed by Gattermann¹ in preparing the lower alkyl urea chlorides.

Some pentadecylamine hydrochloride was heated in an oil-bath to 150° and a slow stream of phosgene passed over it for several hours. A small quantity of liquid was formed, which, when treated with ammonia, gave a substance melting at 109° and identified as monopentadecylurea, thus proving the liquid to be the isocyanate expected. A small amount of dipentadecylurea was also formed, but the greater portion of the amine hydrochloride remained unchanged. As the yield of isocyanate obtained by this method was very unsatisfactory, 4 grams of pentadecylamine hydrochloride and 8 cc. of liquid phosgene were heated together in a sealed tube for ten hours at 100° . On cooling, the excess of phosgene was allowed to escape and a colorless solid mass remained in the tube. This was dissolved in as small a volume as possible of benzene dried by sodium, and the small quantity of unchanged amine hydrochloride was precipitated by dry ligroin. After filtering from the hydrochloride, the benzene and ligroin were distilled while a current of dry hydrogen

¹ Ann. Chem. (Liebig), **244**, 33.

chloride was passed through the flask. A white solid remained, which, after drying on a clay plate for forty minutes in a vacuum desiccator, was analyzed and found to be pure pentadecylurea chloride formed according to:



0.3208 gram at 752.8 mm. and 22° gave 14.5 cc. nitrogen.

	Calculated for $\text{C}_{15}\text{H}_{31}\text{NHCOC}_1$.	Found.
N	4.83	5.07

The urea chloride reacts readily with alcohol and amines. Whereas other urea chlorides as chlorformanilide¹ and chlorformnitranilide² and chlorformmethyl-³ and ethyl amides are quite unstable, decomposing rapidly at 60°–100° into hydrochloric acid and isocyanate, chlorformpentadecylamide, is quite a stable body losing its hydrogen chloride with such difficulty that even after it was heated at 100°–150° for several hours in a stream of dry air, the hydrogen chloride had not been entirely split off. This greater stability of chlorformamides of high molecular weight is probably due to the greater basicity of the compounds on account of the increased positive character of the radical as its weight increases.

Pentadecyl Isocyanate, $\text{C}_{15}\text{H}_{31}\text{NCO}$, was prepared most readily by dissolving the urea chloride in benzene and heating it with calcium oxide, the isocyanate being liberated according to:



When a test showed that the hydrogen chloride had been entirely removed, the solution was filtered from the calcium salts and the benzene distilled, the last traces being removed at reduced pressure. An oil with a slight brownish tint remained. Placed in a freezing-mixture, it solidified and then melted at 8°–14°. All precautions having been taken to prepare the cyanate in a pure condition, it was analyzed without further purification.

0.3192 gram at 745 mm. and 18° gave 15.1 cc. nitrogen.

¹ Heitschel: Ber. d. chem. Ges., **18**, 1178; Lengfeld and Stieglitz: Am. Chem. J., **16**, 75.

² Swartz: Am. Chem. J., **19**, 311; Folin: *Ibid.*, **19**, 338.

³ Gattermann: *Loc. cit.*

	Calculated for $C_{15}H_{31}NCO$.	Found.
N	5.53	5.35

The identity of the isocyanate was confirmed by converting it, by means of aniline, into pentadecylphenylurea.

Pentadecylphenylurea, $C_{15}H_{31}NHCONHC_6H_5$. — Molecular quantities of pentadecyl isocyanate and freshly distilled aniline dissolved in benzene were heated together for a few minutes. After adding a few drops of acetic acid the benzene was distilled off, and the product recrystallized from hot alcohol. The urea melts at 94° .

0.1280 gram gave 0.1276 gram H_2O , and 0.3576 gram CO_2 .

	Calculated for $C_{22}H_{38}N_2O$.	Found.
H	10.98	11.07
C	76.30	76.18

Dipentadecylurea, $(C_{15}H_{31}NH)_2CO$, was obtained in pure condition by heating together 1.1 gram (1 mol.) of pentadecyl isocyanate and 1 gram (1 mol.) of pentadecylamine and recrystallizing from alcohol.

0.3074 gram at 18° and 749.1 mm. gave 15.1 cc. nitrogen.

	Theory for $(C_{15}H_{31}NH)_2CO$.	Found.
N	5.83	5.89

The same substance was also obtained by desulphurizing the thiourea in alcohol solution with mercuric oxide.

Dipentadecylurea is difficulty soluble in hot alcohol; it crystallizes in small needles and melts at 113° .

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOC_2H_5$, was prepared by boiling pentadecyl isocyanate with ethyl alcohol. It is a white crystalline body melting at 54° , and was found to be identical with the urethane obtained by a rearrangement of palmitic amide when bromine and sodium ethylate act upon it in solution in ethyl alcohol, as described below.

Pentadecyl Alcohol, $C_{15}H_{31}OH$.—Ten grams (1 mol.) of pentadecylamine hydrochloride was dissolved in alcohol and 2.6 grams (1 mol.) of sodium nitrite, dissolved in water, added to the solution. Only a small quantity of gas was generated and a white precipitate separated out. A small portion of this precipitate was filtered off and dried on a clay

plate. It was found to decompose with a rapid evolution of gas when heated to 60° . Water was then poured into the flask containing the remaining portion and the mixture boiled until gas ceased to come off. The oil, which was formed, was taken up by ether, and hydrogen chloride gas passed through the ether solution.

A white substance separated out, which was identified as unchanged pentadecylamine hydrochloride. It was found that, if the water solution is kept neutral by adding a few drops of hydrochloric acid from time to time, when necessary, the amine will all be used up in the reaction. After removing the ether by distillation, the alcohol was purified as follows: It was poured into a hot concentrated solution of calcium chloride then taken up by ether, the ether distilled and the residue boiled with water. The oil was again taken up by ether and upon removing the ether, a mixture of oil and solid remained in the flask. By dissolving the mixture in a small quantity of alcohol and placing the flask in a freezing-mixture, the oil remained in solution and the solid crystallized out.

By filtering quickly while cold, a white crystalline body melting at 45° - 46° was obtained, the melting-point agreeing with that obtained by Simonini¹ for pentadecyl alcohol; the greater portion of the product was an oil, which undoubtedly consisted principally of the hydrocarbon, $C_{15}H_{32}$ (see below under undecylamine). The pentadecyl alcohol obtained was further identified by converting it into:

Pentadecyl Phenylcarbamate, $C_6H_5NHCOOC_{15}H_{31}$, which was formed when the alcohol and phenyl isocyanate were mixed together and allowed to remain in a desiccator for twelve hours. As some of the isocyanate remained unchanged, the substance was boiled with water and, in this way, the excess of isocyanate converted into diphenylurea. As diphenylurea is insoluble in ligroin, and the urethane is readily soluble, the two substances were easily separated. For analysis the urethane was recrystallized from ligroin.

0.2668 gram substance at 744.2 mm. and 19° gave 9.6 cc. nitrogen.

¹ Monatshefte, 14, 81.

N	Theory for $C_6H_5NHCOOC_{16}H_{31}$.	Found.
	4.03	4.04

Pentadecylphenylurethane crystallizes in leaflets; it is soluble in all the organic solvents and melts at 72° . On account of its comparatively high melting-point and the ease with which it can be purified, it serves as a better means of identifying pentadecyl alcohol than any other known derivative.

The reactions studied prove conclusively that the amine obtained by distilling pentadecylurethane with slaked lime is the primary normal pentadecylamine, $C_{15}H_{31}NH_2$. In order to find whether the methods described for obtaining urethanes and amines are generally for amides of high molecular weight, the same reactions were carried out with stearic and lauric amides.

Stearic Chloramide, $C_{17}H_{35}CONHCl$, was prepared in the same manner as palmitic chloramide. As stearic amide is very difficultly soluble in cold alcohol, it is difficult to obtain the chloramide free from unchanged amide, from which it could not be separated.

0.2002 gram gave 0.0204 gram chlorine.

Cl	Theory for $C_{17}H_{35}CONHCl$.	Found.
	11.18	10.20

The analysis shows that the product obtained was not absolutely pure. No further effort was made to obtain it in pure condition, but it was further identified by converting it into the urethane, which can easily be separated from the amide by means of ligroin, in which the amide is insoluble. The urethane melts at 63° – 64° and crystallizes in leaflets, and is identical with methylheptadecylurethane obtained by the direct method.

Methyl Heptadecylcarbamate, $C_{17}H_{35}NHCO_2CH_3$, was obtained directly from the amide by means of bromine and sodium methylate in solution in methyl alcohol, as described for preparing methylpentadecylurethane. The yield is 97 per cent of the theoretical. It was purified for analysis by recrystallization from ligroin and alcohol.

0.4584 gram substance gave 19.6 cc. nitrogen at 740.8 mm. and 20.5° .

	Calculated for $C_{17}H_{35}NHCOOCH_3$.	Found.
N	4.47	4.72

Heptadecylamine, $CH_3(CH_2)_{16}NH_2$, was prepared by distilling methylheptadecylurethane with three or four times its weight of slaked lime. Almost a quantitative yield of amine was obtained, 100 grams of amide giving about 82 grams of amine. Turpin¹ obtained only 22 grams of this amine from 100 grams of stearic amide by using aqueous alkali and bromine.

A portion of the amine dissolved in alcohol was evaporated to dryness on the water-bath with concentrated hydrochloric acid. The substance thus obtained is soluble in alcohol, insoluble in ether and decomposes at 200° without melting. It corresponds in every respect with the heptadecylamine hydrochloride obtained by Turpin.

To further identify the amine, the hydrochloride was dissolved in alcohol and evaporated to dryness on the water-bath with the molecular quantity of potassium cyanate, dissolved in water. The body obtained, when recrystallized several times from alcohol, melts at 109° and corresponds in appearance and melting-point to the monoheptadecylurea described by Turpin.

Methyl Undecylcarbamate, $C_{11}H_{23}NHCO_2CH_3$.—To 6 grams (1 equiv.) of lauric amide dissolved in 21 grams of pure methyl alcohol, and 1.4 grams (2 equiv.) of sodium dissolved in 35 grams of methyl alcohol 4.8 grams (2 equiv.) of bromine was added and the mixture boiled for about five minutes. After neutralizing the alkali with acetic acid, the alcohol was distilled and the residue was washed with water, dried, and shaken up with ligroin. A large portion remained undissolved; this was filtered off and the ligroin distilled. A white substance crystallizing in leaflets and melting at 45°–47° (near the melting-point to be expected for a methyl undecylurethane) was obtained. Although this urethane had been prepared in exactly the same manner as the other aliphatic urethanes described above, which were obtained in almost quantitative yield, it was found that, in this case, the yield was only about one-third of the theoretical. The sub-

¹ *Loc. cit.*

stance insoluble in ligroin was then examined and found to have the melting-point 102° , corresponding very closely with that of lauric amide; but when mixed with some of the pure amide, the melting-point was considerably depressed, showing it to be a different substance. This and the high melting-point indicated that the compound might be undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$, of the class of acylureas, whose formation interfered with the application of Hofmann's reaction, in aqueous solution, to higher aliphatic acid amides. This conclusion was verified as described below. For the time being, efforts were directed chiefly to obtaining a better yield of urethane.

In a second experiment the solution of sodium methylate was added in small quantities to the solution of the mixture of bromine and amide. The yield of urethane obtained was no better than before.

The third time the experiment was carried out as follows: 6 grams ($1\frac{1}{4}$ mol.) of bromine was added to 6 grams (1 mol.) of lauric amide dissolved in 27 grams of methyl alcohol, and a solution of 1.8 grams ($2\frac{1}{2}$ atoms) of sodium in 45 grams of methyl alcohol poured at once into the mixture. This time no urea was formed, but a quantitative yield of urethane was obtained. These experiments were repeated a great number of times and in every case, when the entire quantity of sodium methylate was added at once to the solution of the amide and bromine undecylurethane was obtained in excellent yield. If a portion of the solution of sodium methylate was added and but a second elapsed before the remainder was poured into the mixture, the product formed was principally urea.

To obtain the undecylurethane perfectly pure for analysis, it was dissolved in ligroin, in order to separate it from urea and unchanged amide, and then, after removing the ligroin, it was distilled at reduced pressure in an Anschütz distilling-flask.

I. 0.176 gram gave 0.4364 gram CO_2 , and 0.187 gram H_2O .

II. 0.2412 gram gave 0.6008 gram CO_2 , and 0.2588 gram H_2O .

III. 0.3154 gram gave 17.6 cc. nitrogen at 759.5 mm. and 19.5° .

	Calculated for $C_{11}H_{23}NHCOOCH_3$.	I.	Found. II.	III.
C	68.12	67.62	67.93	
H	11.78	11.80	11.92	
N	6.11			6.39

Undecylurethane is but slightly soluble in water and is much more soluble in the organic solvents than the other aliphatic urethanes obtained. It melts at 45° – 47° and can be distilled at reduced pressure without decomposition.

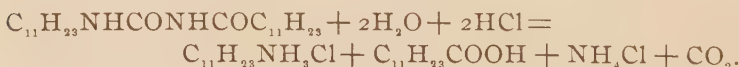
Undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$.—The substance described above as one of the products of the reaction in the first attempt to prepare undecylurethane, was purified by recrystallization from hot ligroin. Analysis showed it to be undecyllaurylurea as expected.

0.2176 gram gave 14.2 cc. nitrogen at 744 mm. and 20° .

	Calculated for $C_{24}H_{48}N_2O_2$.	Found.
N	7.07	7.32

Undecyllaurylurea is difficultly soluble in all the organic solvents in the cold, but dissolves quite readily in hot alcohol. It crystallizes in leaflets and melts at 105° .

To identify the urea more completely it was saponified by heating it with concentrated hydrochloric acid in a sealed tube for five hours at 200° , undecylamine hydrochloride and lauric acid being formed according to :



The undecylamine hydrochloride was recognized by its insolubility in ether; decomposition at 190° without melting and by the urea obtained by treating it with potassium cyanate. The melting-point of the urea (110°) did not change when it was mixed with some of the analyzed specimen of undecylurea.

Normal Undecylamine Hydrochloride, $CH_3(CH_2)_{10}NH_3Cl$.—8 grams of methylundecylurethane were distilled with 28 grams of slaked lime. The product obtained was dissolved in alcohol, concentrated hydrochloric acid added and evaporated to dryness on the water-bath. It was purified by washing it with ether, dissolving it in a small quantity of alcohol and reprecipitating it with ether. Like the other amine hydrochlo-

rides obtained, it is insoluble in ether and decomposes without melting. It crystallizes in bright glistening plates.

I. 0.3246 gram gave 19.9 cc. of nitrogen at 741.5 mm. and 20.5°.

II. 0.2088 gram gave 0.4864 gram CO₂, and 0.2370 gram H₂O.

	Calculated for C ₁₁ H ₂₃ NH ₃ Cl.	I.	Found.	II.
N	6.74	6.87		
C	53.61		63.53	
H	12.53		12.61	

*Undecylamine Chlorplatinat*e, (C₁₁H₂₃NH₃)₂PtCl₆, can be obtained from the amine hydrochloride by dissolving it in alcohol, adding an excess of chlorplatinic acid, and precipitating the chlorplatinat from the alcoholic solution by means of water. The chlorplatinat is a yellow crystalline body, quite soluble in alcohol and insoluble in water. It decomposes when heated to 190°.

0.4468 gram chlorplatinat gave 0.1162 gram platinum.

	Calculated for (C ₁₁ H ₂₃ NH ₃) ₂ PtCl ₆ .	Found.
Pt	25.93	26.03

Undecylamine can be most readily identified by converting the hydrochloride into monoundecylurea. The hydrochloride, best dissolved in alcohol, and a calculated quantity of potassium cyanate, dissolved in a small quantity of water, were mixed together and evaporated to dryness. The product was thoroughly washed with water and recrystallized several times from hot alcohol. It melts at 110° and crystallizes in prismatic needles.

As the body is easily obtained in a pure condition, it serves as the most practical test for undecylamine.

0.1466 gram at 755.2 mm. and 19° gave 17 cc. of nitrogen.

	Calculated for C ₁₁ H ₂₃ NHCONH ₂ .	Found.
N	13.08	13.25

Normal Undecylamine, CH₃(CH₂)₁₀NH₂.—In order to obtain the free amine perfectly pure, the product obtained by distilling methylundecylurethane with lime is treated as follows: The amine is dissolved in ligroin, the solution dried with

solid potassic hydrate and filtered by the use of a siphon filter, and then further dried by heating for about two hours on the water-bath with sodium, and finally distilled over sodium.

As considerable difficulty was experienced in distilling the body on account of its foaming, it was necessary to use a much larger distilling-flask than usual. After distilling the substance from the sodium, a second distillation can be made without any difficulty. A small quantity of the body distilled at 227° – 232° but the greater portion gave a constant boiling-point of 232° .

In making a nitrogen determination, it was necessary to use a very long furnace in order to keep the portion of the tube containing the substance perfectly cold, while the other end was being heated; otherwise the substance was carried over by the carbon dioxide before the tube was sufficiently hot. When cold, the substance existed as a carbonate and in that form it is not volatile.

I. 0.2508 gram substance at 749.7 mm. and 22° gave 21 cc. nitrogen.

II. 0.2642 gram substance at 744.4 mm. and 24° gave 20.6 cc. nitrogen.

	Calculated for $C_{11}H_{23}NH_2$.	I.	Found.
N	8.18	9.31	II. ¹ 8.56

The amine was also dissolved in alcohol and titrated with hydrochloric acid, lacmoid being used as an indicator.

I. 0.1978 gram required 11.35 cc. of $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
11.56 cc.	11.35 cc.

0.2528 gram required 14.58 cc. $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
14.78 cc.	14.58 cc.

At ordinary temperature undecylamine is a colorless liquid; it melts at 15° and boils at 232° under 742 mm. pressure. Like the other amines obtained, it absorbs carbon dioxide and water from the air. In the form of a carbonate it is a white solid.

¹ I was made in a short furnace and II in a long one.

An effort was made to obtain undecylamine directly by the Hofmann method, proceeding as follows: Molecular quantities of bromine and lauric amide, dissolved in a small quantity of alcohol were mixed together and poured into a hot ten per cent solution of caustic potash. A very small quantity of amine was formed, but the principal part of the product was undecyllaurylurea (m.p. 105°).

Benzoylundecylamine, $C_{11}H_{23}NHCOC_6H_5$.—The free amine gives a characteristic benzoyl derivative, which was obtained when a quantity of undecylamine (2 mols.) was dissolved in ether, and the calculated amount of benzoyl chloride (1 mol.) added. The amine hydrochloride formed was filtered, and the ether solution shaken up with a dilute caustic potash solution until no further odor of benzoyl chloride could be detected. After washing with water, the ether was distilled, and the residue dissolved in benzene and precipitated with ligroin.

0.2644 gram at 739 mm. and 20° gave 12.7 cc. of nitrogen.

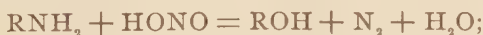
	Calculated for $C_{11}H_{23}NHCOC_6H_5$.	Found.
N	5.09	5.34

Benzoylundecylamine is very soluble in alcohol, ether, and benzene, but difficultly soluble in ligroin. It crystallizes in needles and melts at 60° .

Action of Sodium Nitrite on Undecylamine Hydrochloride.

Normal undecyl alcohol being one of the few unknown primary normal alcohols, and normal undecylamine being easily prepared in quantity, as described above, it was used as a means of obtaining the alcohol. When sodium nitrite acts upon undecylamine hydrochloride secondary reactions take place, besides the usual action of nitrous acid upon the amines.

In trying the action of sodium nitrite upon primary propyl and butyl amines, V. Meyer and Fr. Forster¹ found that four products were obtained. The primary alcohol was formed in the usual manner:



an unsaturated hydrocarbon as follows:

¹ Ber. d. chem. Ges., 9, 529; 10, 130.

$\text{RCH}_2\text{CH}_2\text{NH}_2 + \text{HONO} \rightarrow \text{RCH}=\text{CH}_2 + \text{N}_2 + 2\text{H}_2\text{O}$;
a secondary alcohol by addition of water to the unsaturated hydrocarbon,



and a nitrosodialkylamine whose method of formation was explained by Linnemann,¹ who had previously obtained the same body by the same reaction. He assumes that amine nitrite is formed as an intermediate product, the formation of the nitrosamine then taking place according to the equation:²



There is reason to believe, that, when sodium nitrite acts upon undecylamine, corresponding products are formed, although but two of them were thoroughly investigated.

Normal Undecyl Alcohol, $\text{CH}_3(\text{CH}_2)_{10}\text{OH}$.—Equivalent quantities of undecylamine hydrochloride dissolved in alcohol and sodium nitrite dissolved in water, were mixed together. A white precipitate was immediately deposited, which, when filtered off and dried, was found to decompose at 60° with evolution of gas. To obtain the alcohol the amine hydrochloride and sodium nitrite in solution in water were allowed to boil gently until gas ceased to be generated, care being taken to keep the solution neutral by adding a few drops of hydrochloric acid whenever a test showed it to be alkaline.

The oil formed was taken up by ether, and the solution dried by solid potassic hydrate. After removing the ether, the oil was distilled at reduced pressure. Four fractions were collected, about one-fourth of the product boiling at 84° – 90° ; a small quantity at 90° – 118° ; about one-third at 118° – 126° , and the remainder about 126° . Upon redistilling the third fraction, the greater portion of it boiled at 123° . This boiling-point is lower than that expected for and alcohol occupying such a place in the series and analysis showed it to be still impure.

¹ Ann. Chem. (Liebig), **162**, 3.

² The formation of a derivative of a dialkylamine in this reaction points to the intermediate formation of a diazo body $\text{RCH}(\text{N}_2)$ which could alkylate a second molecule of the amine as easily as diazomethane methylates. The same diazo body would give with water the primary alcohol. The formation of a hydrocarbon $\text{RCH}=\text{CH}_2$, and particularly of a secondary alcohol, RCHOHCH_3 , from a primary

amine points to isomeric diazo-bodies $\begin{array}{c} \text{RCH}-\text{CH}_2 \\ | \quad | \\ \text{N} \quad \text{N} \end{array}$ whose discovery and investigation will probably be only a question of time.

I. 0.3866 gram gave 1.025 gram CO_2 , and 0.4440 gram H_2O .

II. 0.1928 gram gave 0.5198 gram CO_2 , and 0.223 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{23}\text{OH}$	I.	Found.	II.
C	76.74	72.3		73.52
H	13.96	12.76		12.79

While the above figures are low for undecyl alcohol, yet they show that the body can be nothing but the alcohol in an impure condition. The alcohol was then further purified by converting it into undecylphenylurethane, which being a solid can be recrystallized until it gives a constant melting-point. By saponification the urethane yields the undecyl alcohol free from the hydrocarbon (see below) accompanying it, by the above method of preparation. The urethane also furnishes an excellent means of identifying the alcohol.

Normal Undecyl Phenylcarbamate, $\text{C}_6\text{H}_5\text{NHCO}_2\text{C}_{11}\text{H}_{23}$.—Six grams of the crude undecyl alcohol and 4.1 grams of phenyl isocyanate were mixed together in a flask and allowed to remain in a desiccator over night. The compound formed was dissolved in ligroin to remove any diphenylurea that might be present. After filtering, distilling off the ligroin, and recrystallizing from alcohol a number of times, a substance was obtained showing the constant melting-point 62° and crystallizing in needles.

0.2852 gram gave 12.9 cc. nitrogen at 755.7 mm. and 22° .

	Calculated for $\text{C}_6\text{H}_5\text{NHCO}_2\text{C}_{11}\text{H}_{23}$.	Found.
N	4.81	5.10

In order to convert undecylphenylurethane back into the alcohol, it was boiled for two hours with alcoholic potash. The solution was then poured into dilute acid, the oil taken up by ether, and the ether solution thoroughly washed with water, then dried for twenty-four hours with freshly-heated potassium carbonate. The alcohol remaining after removing the ether was then distilled under reduced pressure. The body when purified as described boiled at 131° , at 15° mm. pressure, and melted at 19° . Although both boiling-point

and melting-point are those expected for undecyl alcohol, the figures obtained in analyzing the body were still a little low, showing a slight impurity.

0.2466 gram gave 0.6828 gram CO_2 , and 0.2964 gram H_2O .

	Calculated for $\text{C}_{11}\text{H}_{23}\text{OH}$.	Found.
C	76.74	75.51
H	13.95	13.35

In order to determine whether the alcohol obtained was the primary or secondary (see above), it was oxidized by taking one part of the alcohol, two of potassium bichromate, three of sulphuric acid and nine of water, and boiling the mixture gently under an inverted condenser for twenty hours. The resulting product was extracted with ether, and the ether extract washed with water. After removing the ether by distillation, the residue was dissolved in alcohol and when the flask containing the solution was placed in a freezing-mixture, white crystals were formed. The crystals were filtered in a funnel surrounded by a freezing-mixture. The body had an acid reaction, and melted at 26° .

The silver salt was prepared by suspending the acid in water, neutralizing with ammonia and adding an excess of silver nitrate. The salt was washed, first with water, then with a small quantity of alcohol.

0.1602 gram gave 0.0577 gram silver.

	Calculated for $\text{C}_{11}\text{H}_{21}\text{O}_2\text{Ag}$.	Found.
Ag	36.86	36.01

The analysis of the silver salt, as well as the melting-point (26°), shows the oxidation product to be normal undecylic acid (m. p. 28.5°); consequently the substance from which it was obtained, must have been the hitherto unknown primary normal undecyl alcohol.

Undecylene, $\text{CH}_3(\text{CH}_2)_8\text{CH} : \text{CH}_2$.—The fraction boiling below 90° , which was obtained by distilling the product formed by the action of sodium nitrite on undecylamine hydrochloride, was redistilled. The greater portion of the product boiled at 84° at 18 mm. pressure.

0.1754 gram gave 0.5394 gram CO_2 , and 0.225 gram H_2O .

	Calculated for $C_{11}H_{22}$.	Found.
C	85.71	83.86
H	14.28	14.25

As the analysis showed that the substance was not quite pure, it was converted into the dibromide, the boiling-point of which is so much higher than that of any of the other products that might be present, that there could be no difficulty in separating it from them by distillation.

Undecylene Dibromide, $CH_3(CH_2)_8CHBrCH_2Br$.—The undecylene (b.p. 84° , 18 mm.) was cooled in a freezing-mixture, and the calculated amount of bromine diluted by three and a half times its volume of carbon disulphide, added drop by drop. After removing the carbon disulphide, the heavy oil was distilled at reduced pressure. At 18 mm. it showed the constant boiling-point 161° .

A bromine determination by the Carius method gave the following results:

0.2068 gram substance gave 0.2490 gram AgBr.

	Calculated for $C_{11}H_{22}Br_2$.	Found.
Br	50.95	51.23

Nothing further was done with the second and fourth fractions excepting that a test showed the fourth fraction to be rich in nitrogen, the principal object of the study of the reaction being to determine whether the method could be used for preparing undecyl alcohol. Although undecyl alcohol is formed according to the equation,

$C_{11}H_{23}NH_2Cl + NaONO = C_{11}H_{23}OH + N_2 + NaCl + H_2O$,
the method is not to be recommended, as the yield obtained is very small, and it is very difficult to separate the alcohol from the other products of the reaction.

*Preparation of Urethanes Directly from Acid Amides
Dissolved in Ethyl Alcohol.*

The yield of urethanes obtained by treating an acid amide dissolved in ethyl alcohol with sodium ethylate and bromine, is somewhat lower than that obtained when methyl alcohol is used as the solvent, yet, in every case in which the method has been tried, it is much higher than that obtained by the older method.

Ethyl Phenylcarbamate, $C_6H_5NHCO_2C_2H_5$.—The yield of ethylphenylurethane obtained by Swartz by treating dry benzobromamide with sodium ethylate was only 15 per cent of the theoretical, the remainder of the product being phenylbenzoylurea and unchanged amide. By proceeding in the following manner, a yield corresponding to 70 per cent of the theoretical was obtained.

5.7 grams (3 atoms) of sodium were dissolved in 142 grams of ethyl alcohol and the solution poured into a mixture of 10 grams (1 mol.) of benzamide, dissolved in 85 grams of ethyl alcohol, and 19 grams ($1\frac{1}{2}$ mols.) of bromine. The mixture was boiled for a few minutes on the water-bath, the alcohol distilled and the residue washed with water. After the product was thoroughly dried on a clay plate, it was distilled at reduced pressure. 9.6 grams of pure ethylphenylurethane were obtained, melting at 52° .

Ethyl-m-Nitrophenylcarbamate, $m\text{-NO}_2C_6H_4NHCO_2C_2H_5$.—By the older method Swartz obtained 6 per cent of ethyl-*m*-nitrophenylurethane and 53 per cent of nitrobenzoylphenylurea. By proceeding as in the last case 56 per cent of urethane was obtained with a considerable quantity of unchanged amide, but no urea.

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCO_2C_2H_5$.—2.7 grams (3 atoms) of sodium, dissolved in 65 grams of ethyl alcohol, were poured into a mixture of 9.3 grams ($1\frac{1}{2}$ mols.) of bromine and 10 grams (1 mol.) of palmitic amide, dissolved in 40 grams of ethyl alcohol. After heating the mixture for a few minutes on the water-bath, a few drops of acetic acid were added and the alcohol distilled. The residue was washed with water, dissolved in ligroin and the undissolved portion filtered off. After removing the ligroin, the substance was distilled at 14 mm. pressure. It boils at 225° (14 mm.), and melts at 54° . It corresponds in every respect with the urethane obtained by me synthetically. The yield is 50 per cent of the calculated.

0.4838 gram at 749.5 mm. and 16° gave 21 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCO_2C_2H_5$.	Found.
N	4.68	4.99

As in so many cases ureas were formed with such remarkable ease in the presence of alcohol (see undecyllaurylurea), some experiments were tried in order to find out whether they could be obtained by the direct action of an isocyanate upon an amide in alcoholic solution.

1. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 8 grams of methyl alcohol, 1 gram (1 mol.) of phenyl isocyanate was added, and the mixture heated for about five minutes on the water-bath. The products obtained, when purified, were identified as unchanged amide and phenylmethylurethane.

2. To 1 gram of benzamide in a 10 per cent caustic potash solution, 1 gram of phenyl isocyanate was added, and the mixture shaken up until the odor of isocyanate disappeared. The products obtained were diphenylurea (m. p. 235°) and unchanged amide.

3. 1.3 grams (1 mol.) of phenylurea chloride was added to 1 gram (1 mol.) of benzamide, dissolved in 12 grams of methyl alcohol, and the mixture heated for a few minutes on the water-bath. The odor of benzoic ether was quite noticeable, the other products obtained being ammonium chloride and phenylmethylurethane.

4. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 4 grams of methyl alcohol and 0.3 gram of sodium dissolved in 8 grams of methyl alcohol, 1.3 grams (1 mol.) of phenylurea chloride were added. The products obtained were benzamide and methylphenylurethane.

As not the slightest trace of phenylbenzoylurea was obtained in any of the above experiments, it is quite evident that an isocyanate, in its ordinary condition, does not act upon an amide as readily as upon an alcohol.

Action of Sodium Methylate and Bromine on Cinnamic Amide.

To a mixture of 8 grams of cinnamic amide dissolved in 45 grams of methyl alcohol, and 2.7 grams (2 atoms) of sodium, dissolved in 70 grams of methyl alcohol, 8.7 grams of bromine were added in small portions at a time. The mixture was heated for a short time on the water-bath, and after adding a

few drops of acetic acid, the alcohol was allowed to evaporate spontaneously. The product remaining was shaken up with ether. A portion dissolved, but a considerable quantity remained undissolved. The undissolved portion was washed with water to remove the sodium bromide, and for analysis it was recrystallized two or three times from alcohol. The body melts at 218° with decomposition.

I. 0.1566 gram gave 7.5 cc. nitrogen at 747.5 mm. and 16° .

II. 0.1402 gram gave 0.2358 gram of CO_2 , and 0.0618 gram H_2O .

	Calculated for $\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Br}$.	Found.
C	46.51	45.86
H	4.65	4.89
N	5.42	5.49

The presence of considerable bromine in the compound was proved by a qualitative test. No rearrangement had taken place, as the body, when heated with a solution of caustic potash, gave off ammonia, showing that the amidogroup had remained unchanged. No effort was made to determine the constitution of the body, but in all probability the constitutional formula is $\text{C}_6\text{H}_4\text{CHBrCH}(\text{OCH}_3)\text{CONH}_2$, or possibly with the bromine and methoxy group exchanged.

From the ether solution a thick pasty substance was obtained which could not, by any means employed, be crystallized, and as it decomposed when distilled *in vacuo*, it was not obtained sufficiently pure for analysis.

Action of Sodium Methylate and Bromine upon Salicylic Amide.

McCoy¹ in treating salicylic amide with bromine and alkali in solution in water according to Hofmann's reaction, found that the benzene ring is brominated twice before the rearrangement is effected. The same reaction when tried by me in methyl alcohol, gave the same result. The experiment was carried out as follows:

To a mixture of 10 grams (1 mol.) of salicylic amide, dissolved in 66 grams of methyl alcohol and 5 grams (3 atoms) of sodium, dissolved in 110 grams of methyl alcohol, 11.6 grams (1 mol.) of bromine were added. The product obtained was identified as dibromosalicylic amide melting at 183° .

¹ Am. Chem. J., 21, 116.

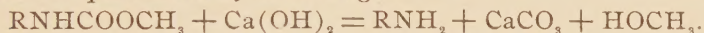
It is evident that the method of preparing urethanes, described in this paper, cannot on account of the reactivity of the reagents, be used to effect a rearrangement of bodies analogous to salicylic or cinnamic amide. In such cases the method of Curtius¹ is the most satisfactory.

The results of the work described in this paper and the conclusions to be drawn from them can be briefly summarized as follows :

1. Urethanes are obtained without the isolation of the brom- or chloramides by the action of a sodium alcoholate on a mixture of an acid amide and bromine.

The method is applicable to the preparation of both aromatic and aliphatic urethanes, in ethyl and methyl alcohol solution, but cannot be used when the acid amide is unsaturated or otherwise very susceptible to bromine.

2. The urethanes, when distilled with slaked lime, give amines quantitatively according to



As the urethanes were also obtained in excellent yield, this method was found to be a practical one for the preparation of higher aliphatic amines.

3. The amines, obtained by the above-described method, are primary monoalkylamines as shown : (a) by the preparation of a mustard oil and an isocyanate from pentadecylamine; (b) by the formation of primary alcohols when sodium nitrite was allowed to act upon the amine hydrochlorides.

4. The formation of acyl alkylureas in applying the Hofmann reaction in aqueous or alcoholic solution takes place whenever, owing to the slowness of the reaction, considerable unchanged acid amide is present, while the remainder of the acid amide is suffering "rearrangement"; the rearranged portion then acts upon the unchanged amide even in the presence of alcohol or water and forms a urea.

5. Experiments show that an isocyanate in its ordinary condition, will not act upon an acid amide in the presence of alcohol or water.

I wish here to express my sincere thanks to Professor Stieglitz, who directed and advised me in this work.

¹ J. prakt. Chem., **52**, 227, 433.

